COVALENT BONDING EFFECT ON THE MEAN EXCITATION ENERGY OF H_2 WITH THE LOCAL PLASMA MODEL

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Chemical bonding is taken into account explicitly in the determination of the mean excitation energy (I) for stopping power of H_2 with the local plasma approximation by employing molecular electronic wave functions for H_2 for the first time. This procedure leads to a new value for I_{H_2} that is higher than all accepted experimental and theoretical values.

Recently research was initiated to investigate chemical effects on the electronic stopping power [1,2]. Because of the simplicity of the local plasma approximation for the determination of the mean excitation energy for stopping power research was initiated so that the equation for the logarithmic mean excitation energy (1) according to the local plasma approximation [1–3],

$$I = \gamma \exp \left(\frac{1}{Z} \int \rho(r) \ln[\hbar \omega_p(r)] \, d^3r \right) , \qquad (1)$$

could be applied with the use of accurate electronic wave functions that account for chemical binding to describe the local electron number density in the gas phase and in the solid phase, for ionic solids and especially for metals. In eq. (1) Z is the number of electrons per particle (the atomic number for atoms) of target matter, $\rho(r)$ is the local electron density, $\omega_p(r)$ is the plasma frequency, $\hbar$ is Planck's constant divided by 2π and γ is a constant introduced to adjust the contribution from the collective modes of longitudinal electronic oscillations to the effective frequency (ω). The plasma frequency and the effective frequency are functions of the local electron density:

$$\omega = \gamma \omega_p(r) = \gamma [4\pi e^2 \rho(r)/m]^{1/2} . \qquad (2)$$

In this work such a new application of the local plasma approximation to determine I of gas phase molecules is described. It consists in employing avail-able very accurate molecular electronic wave functions to determine the function of the required local electron number density of diatomic and small polyatomic molecules starting with H_2, which subsequently is employed to determine the value of the molecular logarithmic mean excitation energy with the local plasma model using eq. (1). The application of this empirical model has the advantage of great simplicity compared to the application of the models that require knowledge of the electric dipole oscillator strengths (or distributions). The local electron number density, $\rho(r)$, for a diatomic molecule with n electrons in a stationary state is defined by

$$\rho(r) = \sum_{i=1}^{n} \int |\Psi(r_1, s_1, r_2, s_2, ..., r_i, s_i, ..., r_n, s_n; R|^2$$

$$\times \delta(r - r_i) d^3r_1 ds_1 d^3r_2 ds_2 ... d^3r_n ds_n , \qquad (3)$$

where r_i and s_i are the space and spin coordinates of the ith electron, R is the internuclear distance of the diatomic molecule, and $\Psi(r_1, s_1, r_2, s_2, ..., r_i s_i, ..., r_n, s_n; R)$ designates the time-independent electronic wave function of the system of n electrons.

In these first calculations for homonuclear molecules with this model, the molecular electronic wave functions employed are: (i), the 13-term electronic wave function for H_2 at its equilibrium internuclear distance (1.4 bohr) of James and Coolidge [4], that was reported to yield a dissociation energy of 4.697

eV compared with the present experimental value of 4.75 eV; (ii), a more recent molecular electronic wave function for H_2 at its internuclear equilibrium distance (1.4 bohr) with a three-term closed shell correlation function by Kołos and Roothaan [5] that is reported to yield a dissociation energy of 4.6955 eV; and (iii), another accurate molecular electronic wave function for H_2 with 12 terms by Kołos and Roothaan [6] that yielded a dissociation energy of 4.7397 eV at 1.4 bohr internuclear distance. The use of these molecular wave functions led to the computation of $\rho(r)$ with eq. (3) and, with eq. (1) of the local plasma approximation for $\gamma = 1$, to the computation of the values 20.3 eV, 19.5 eV, and 20.2 eV for I_{H_2} respectively. These numbers are expected to be correct within less than 5% error as a result of approximations and possible nonconvergence to the correct values.

In order to determine the correct value for I_{H_2} the value of γ has to be determined. Once the value of γ has been determined the correct value of I is equal to the product of γ times $I_{\gamma=1}$, the value of I for $\gamma = 1$, as follows from eq. (1). Effective values of γ for atoms were determined by direct comparison of atomic I values from this model with those from the method of moments of the oscillator strength distribution [7–9]. It has been reported [7–9] that eq. (1) led to *low* values of I for atoms with [10] $\gamma = 1$, and to values of I for atoms with [11] $\gamma = 2^{1/2}$ that were *higher* by 20–30% compared to the corresponding atomic values obtained with the method of moments of electric dipole oscillator strength distributions [7,8]. Therefore, the effective value of γ for atoms, which is the measure of the shift of the effective frequency from the plasma frequency in eq. (2), turns out to be between 1 and $2^{1/2}$ for all atoms up to Sr for which accurate values of I have been calculated [7,8].

Of course, here it is not an atom, but a covalently bonded molecule that is treated. Nevertheless, a similar approach, namely, to consider the value of 19.26 eV from the model of moments [12] with semiempirical data as the correct value for I_{H_2} and to determine γ for H_2 from the ratio of I for the two models, perhaps an easy way out, was dismissed as being a priori prejudicial to either model. I decided to examine the theoretical results for I of atoms more closely instead, lest these should provide any useful independent evidence to be used for or against either model.

Table 1 shows effective values of γ for atoms cal-

Table 1
Values of the constant γ for atoms of several elements obtained with various electronic wave functions for atoms.

Atom	γ_{SL}	γ_{HF-HS}	γ_{HFS}	$\gamma_{exact \, w/f}$
H(1)				1.235
He(2)	1.03(1)	1.12(3)	1.09(7)	
Li(3)	1.27(7)	1.24(3)	1.29(6)	
Be(4)	1.20(5)	1.19(8)	1.22(6)	
B(5)	1.21(0)	1.22(2)	1.24(7)	
C(6)	1.18(2)	1.21(8)	1.24(0)	
N(7)	1.14(7)	1.20(5)	1.22(4)	
O(8)	1.13(3)	1.19(0)	1.22(7)	
F(9)	1.10(4)	1.17(6)	1.22(0)	
Ne(10)	1.07(5)	1.16(0)		

culated from the ratio of the accurate values of I as determined from the model of moments [7–9] over those from the local plasma model using, (i), electron densities determined with Slater orbitals [13] (SL), in this work, (ii), electron densities tabulated by Herman and Skillman, based on Hartree–Fock wave functions (HF–HS) [14], from previous work [11,15], and (iii), electron densities determined with Hartree–Fock–Slater orbitals (HFS), in this work. The latter orbitals were determined by Clementi and Roetti [16].

The difference between the SL and HFS atomic γ values in table 1 is ascribed to the differences in the wave functions used. Possibly, the same is true for the HF–HS values of γ.

The calculations with Hartree–Fock wave functions, along with SCF (self consistent field) wave functions, however to a limited sense, lead to values for quantities like, e.g., electron densities that are considered valid to "second order" as a result of the early investigations of Brillouin [17], and Møller and Plesset [18]. The Hartree–Fock–Slater (HFS) γ values in table 1 are considered to be the most reliable. These atomic γ values show practically no difference between γ for the lighter atoms and the heavier atoms with the exception of He and to some extent Li, contrary to the early assignment [3] of the value of 1 for the light atoms and of $2^{1/2}$ for the heavy atoms. The lower γ for He is due to an underestimation, of I_{He} as already suggested by Dehmer et al [7]. Indeed this value [7] of I_{He} is about 9% smaller than the closest experimental value [7], while for other noble gases the corresponding difference from experimental values is about a few percent. Incidentally, the value of

I_{He} determined with the local plasma model [11] is shown smaller by $\approx 10\%$ in fig. 9 of ref. [7], and this slight misrepresentation has apparently been carried over in fig. 4 of ref. [19].

It should be noted that the results for I_{He} with the local plasma model in this work reinforce its predictive capacity [7–9] for the semiempirical determination of I further. Ref. [9] contains critical discussions about the model and its consequences.

Since in table 1 even for larger atoms than H the effective γ value is ≈ 1.22 – with the exception of He and to a lesser extent of Li – it may be considered not untenable to ascribe a similar value of γ to light molecules like H_2 since, in addition, no distinction between atoms and molecules was made by Lindhard and Scharff in their model [3]. After all the local electron density difference is small – albeit extremely important to chemical bonding – between molecules and their constituent [20] atoms (or ions) compared to the local electron density of the constituents of the molecule in all areas, except in the internuclear region, where, however, the electron density is many times smaller compared to theat around the nuclei. As for the nuclear charge distribution both in a molecule and in the constituent atoms (or ions), the distribution deviates similarly from that of a uniform fixed background of positive charge assumed in the statistical models. Therefore the shift in the effective frequency in eq. (2) in going from the independent particle model to the statistical atomic model may be considered approximately equal to the shift from the independent molecule model to the statistical "molecular" model. Such an assignment, i.e. $\gamma \approx 1.2$, would certainly lead to a value of I for H_2 well *over* 20 eV. Indeed, if the value of 19.5 eV is accepted for I_{H_2} with $\gamma = 1$, the value for $\gamma \approx 1.2$ would yield 23.4 eV. Of course this value is based on the static electron density at the equilibrium nuclear distance. However, when the effect of the internal motion of the molecule on the electron density is taken into account, this figure may become somewhat lower, roughly ≈ 23 eV, in view of the already reported [21] decrease of I_{H_2} from 19.52 to 19.21 eV when thermal averaging over rotational levels at the ground vibrational level of H_2 was taken into account in the calculation of I_{H_2} with the method of sums.

There are several values [2,15,19] for I_{H_2} in addition to the values mentioned earlier in this work. It is interesting that the originators [3] of this statistical model treated the case of molecular hydrogen using an atomic wave function, however, with Z set equal to 1.2 to account for chemical bonding, and γ set equal to 1. The value of 16 eV that they obtained [3] compared excellently with the experimental values accepted [3] at that time. Nevertheless the value of 16 eV for I_{H_2} was lower in relation to the theoretical values [2,3].

Certainly the value of ≈ 23 eV for I_{H_2} agrees with none of the previously reported theoretical values [2,12,19,21]. However, it is close to or within the upper limit of some of the reported experimental values [2] when the reported experimental error is considered. This is of course very weak support, in view also of the large number of all the previous theoretical calculations and the recent experimental determination [22] of I_{H_2} that lead to a value lower than 19.5 eV for I_{H_2}.

However, further investigation of experimental I_{H_2} values shows [23] that the latest experimental I_{H_2} values [22,23] (17.6 eV) resulted from the application of shell corrections to the experimental stopping cross section of H_2, which were of very much larger magnitude and of opposite sign compared to those in any previous investigation [15,24–26] for H_2. If, instead, the previous shell corrections are applied to these data, the I_{H_2} values become [23] much larger and include even values above 20 eV: $\geqslant 20.3$ eV for [27] 585 keV and $\geqslant 20.4$ eV for [22] 700 keV protons with corresponding upper limits for I_{H_2} of $\geqslant 22.5$ eV and $\geqslant 21.3$ eV, respectively, due to the reported [22,27] experimental error. In addition, re-examination of previous experimental stopping cross-section values [28] [+1] of H_2 for protons showed [23] *average* values of over 21 eV for I_{H_2}. In fact the majority of the experimental data in the lase ≈ 20 yr supports a value [23] for I_{H_2} over 20 eV.

Definitely a thorough investigation is warranted on

[+1] There is significant disagreement between the value for the stopping cross section of H_2 for 0.3111 MeV protons in table 2 and fig. 4 therein, probably due to a misprint. The value in the figure is much more consistent with the rest of the data and the reported error. The erroneous value has apparently eluded attention and appeared in recent publications [24,26,27]. In a subsequent communication Dr. R.A. Langley kindly confirmed that the correct value should be 5.54 instead of 4.54.

the basis also of these findings that surprisingly support a higher I_{H_2} value than 20 eV, which is supported by this application of the local plasma model that considers also the effect of chemical bonding.

It should be noted that even if it turns out that for some reason (e.g., the empirical origin of this [2,9] statistical model) this model leads to too high a value for I_{H_2} for $\gamma \approx 1.22$, it will still be very interesting how for $\gamma = 1$ it leads to $I_{H_2} \leqslant 19.5$ eV in agreement with the accepted theoretical values [12,21], when the covalent bonding in H_2 is taken into account in this work for the first time in this application of the local plasma model for a homonuclear diatomic molecule.

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